

[54] PROCESS FOR THE PREPARATION OF A POLYOLEFIN, AND A CATALYST FOR THIS PROCESS

[75] Inventors: Joachim Berthold, Eppstein; Bernd Diedrich, Eschborn; Rainer Franke, Niedernhausen; Jürgen Hartlapp, Hattersheim am Main; Werner Schäfer; Wolfgang Strobel, both of Hofheim am Taunus, all of Fed. Rep. of Germany

[73] Assignee: Hoechst Aktiengesellschaft, Fed. Rep. of Germany

[21] Appl. No.: 388,023

[22] Filed: Jun. 14, 1982

[30] Foreign Application Priority Data Jun. 20, 1981 [DE] Fed. Rep. of Germany 3124223

[51] Int. Cl.³ C08F 4/02; C08F 10/02

[52] U.S. Cl. 526/124; 526/125; 526/352; 526/348.3; 526/348.5; 526/348.6; 526/901; 502/154

[58] Field of Search 526/124, 125

[56] References Cited U.S. PATENT DOCUMENTS 3,644,318 2/1972 Diedrich et al. 526/124 4,224,183 9/1980 Staiger 526/124 4,250,284 2/1981 Dilbouille et al. 526/124

Primary Examiner—Edward J. Smith Attorney, Agent, or Firm—Connolly and Hutz

[57] ABSTRACT Polyolefins having a broad molecular weight distribution are obtained in a very high yield even using, as the catalyst, a product from the reaction of a magnesium alcoholate with titanium tetrachloride, if the reaction between the magnesium alcoholate and the titanium tetrachloride is carried out at a relatively low temperature and the reaction mixture is then heated to a fairly high temperature in order to split off alkyl chlorides.

3 Claims, No Drawings

PROCESS FOR THE PREPARATION OF A POLYOLEFIN, AND A CATALYST FOR THIS PROCESS

Processes are known for the preparation of polyolefins by means of catalysts which are formed by reacting magnesium alcoholates and/or complex magnesium alcoholates with transition metal halides. (German Auslegeschriften Nos. 1,795,197 and 1,957,679 and German Offenlegungsschrift No. 2,000,566).

In one case, a temperature range of 0° to 200° C. is recommended for the reaction of the magnesium compound and the chlorine-containing titanium compound, but the upper temperature limit should be so chosen that no decomposition products are formed. In addition to the high activity of the polymerization catalysts, it is mentioned as a special advantage that it is possible to prepare ethylene homopolymers and ethylene/ α -olefin copolymers which have a narrow molecular weight distribution (German Auslegeschriften Nos. 1,795,197 and 1,957,679).

In another case, the reaction of the metal alcoholate with the transition metal compound is carried out in the presence or absence of an inert diluent at temperatures of 40° to 210° C.; the duration of the reaction is, in general, between 5 and 240 minutes (German Offenlegungsschrift No. 2,000,566). An express warning is given against a longer reaction time, since it is alleged to cause an impairment of the properties of the catalyst. In this publication too, it is mentioned as an advantage of the catalysts that they have a high activity and that it is possible to prepare polyolefins which have a narrow molecular weight distribution. A catalyst which is obtained by reacting magnesium ethylate with vanadium tetrachloride and which produces a polyethylene having a broad molecular weight distribution is described at the same time. However, vanadium compounds have the great disadvantage that, in contrast with titanium compounds, they are extremely toxic. Products containing vanadium compounds can, therefore, only be employed to a limited extent. In addition, high costs are incurred in working up the catalyst mother liquors if vanadium compounds are employed in industrial polymerization processes.

The problem was therefore presented of finding polymerization catalysts based on a magnesium alcoholate, by means of which polyolefins having a broad molecular weight distribution can be prepared in a high yield.

It has now been found that polyolefins having a broad molecular weight distribution can be obtained in a very high yield even using the products of the reaction of magnesium alcoholates with titanium tetrachloride, if the reaction between the magnesium alcoholate and the titanium tetrachloride is carried out at a relatively low temperature and the reaction mixture is then subjected to a heat treatment at a fairly high temperature in order to split off alkyl chlorides.

The invention relates therefore to a process for the polymerization of a 1-olefin of the formula $R^4CH=CH_2$ in which R^4 denotes hydrogen or an alkyl radical having 1 to 10 carbon atoms, in the presence of a catalyst composed of the product from the reaction of a magnesium alcoholate with titanium tetrachloride (component A) and an organometallic compound of Groups I to III of the periodic system (component B), which comprises carrying out the polymerization in the presence of a catalyst in which the component A has

been prepared by a procedure in which, in a first reaction stage, a magnesium alcoholate has been reacted with titanium tetrachloride in a hydrocarbon at a temperature of 50° to 100° C., the reaction mixture formed is subjected, in a second reaction stage, to a heat treatment at a temperature of 110° to 200° C., until no further alkyl chloride is split off, and the solid is then freed from soluble reaction products by washing several times with a hydrocarbon.

The invention also relates, however, to the catalyst used for this process and to its preparation.

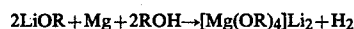
A magnesium alcoholate is used for the preparation of the component A. This magnesium alcoholate can be a "simple" magnesium alcoholate of the formula $Mg(OR)_2$ in which R denotes identical or different alkyl radicals having 1 to 6 carbon atoms. Examples are $Mg(OC_2H_5)_2$, $Mg(OiC_3H_7)_2$, $Mg(OnC_3H_7)_2$, $Mg(OnC_4H_9)_2$, $Mg(OCH_3)(OC_2H_5)$ and $Mg(OC_2H_5)(OnC_3H_7)$. It is also possible to use a "simple" magnesium alcoholate of the formula $Mg(OR)_nX_m$ in which X is halogen, $(SO_4)_{\frac{1}{2}}$, OH, $(CO_3)_{\frac{1}{2}}$, $(PO_4)_{\frac{1}{2}}$ and Cl, R has the meaning mentioned above and $n+m$ is 2.

It is also possible, however, to employ a "complex" magnesium alcoholate. The term "complex" magnesium alcoholate describes a magnesium alcoholate which, as well as magnesium, contains at least one metal of the 1st to 4th main group of the periodic system. The following are examples of a complex magnesium alcoholate of this type: $[Mg(OiC_3H_7)_4]Li_2$; $[Al_2(OiC_3H_7)_8]Mg$; $[Si(OC_2H_5)_6]Mg$; $[Mg(OC_2H_5)_3]Na$; $[Al_2(OiC_4H_9)_8]Mg$; and $[Al_2(O-secC_4H_9)_6(OC_2H_5)_2]Mg$. The complex magnesium alcoholates (alkoxo salts) are prepared by known methods (literature references: Meerwein; Ann. 455 (1927), page 234 and 476 (1929), page 113; HoubenWeyl, Methoden der organischen Chemie ["Methods of organic chemistry"], volume 6/2, page 30). The following examples of the preparation of the complex magnesium alcoholate may be mentioned:

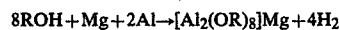
1. Two metal alcoholates are allowed to act on one another in a suitable solvent, for example



2. Magnesium is dissolved in an alcoholic solution of a metal alcoholate



3. Two metals are dissolved in alcohol simultaneously



The simple magnesium alcoholates, in particular $Mg(OC_2H_5)_2$, $Mg(OnC_3H_7)_2$ and $Mg(OiC_3H_7)_2$ are preferably used. The magnesium alcoholate is employed in a pure form or fixed on a support.

The preparation of the component A is effected in two reaction stages at different temperatures.

In the first reaction stage, the magnesium alcoholate is reacted with titanium tetrachloride at a temperature of 50° to 100° C., preferably 60° to 90° C., in the presence of an inert hydrocarbon and while stirring. 1 to 5 moles of titanium tetrachloride are employed for 1 mole of magnesium alcoholate, preferably 1.4 to 3.5 mole of titanium tetrachloride for 1 mole of magnesium alcoholate.

A suitable inert hydrocarbon is an aliphatic or cycloaliphatic hydrocarbon, such as butane, pentane, hexane, heptane, isooctane, cyclohexane or methylcyclohexane,

and an aromatic hydrocarbon, such as toluene or xylene; it is also possible to use a hydrogenated diesel oil or gasoline fraction which has been carefully freed from oxygen, sulfur compounds and moisture.

The reaction time in the first stage is 0.5 to 8 hours, preferably 2 to 6 hours.

A substantial replacement of the alkoxy groups of the magnesium alcoholate by the chlorine atoms of the titanium tetrachloride takes place in the first reaction stage. The reaction product obtained in this stage is a solid which is insoluble in hydrocarbons and contains magnesium and titanium, and titanium compounds which are soluble in hydrocarbons and contain chlorine and alkoxy groups.

In the second reaction stage, the resulting reaction mixture is subjected to a heat treatment at a temperature of 110° to 200° C., preferably 110° to 160° C., while stirring. During this heat treatment, the titanium content of the hydrocarbon-insoluble solid increases greatly and alkyl chlorides are split off. It is assumed that the soluble titanium alkoxychlorides are converted, by the splitting off of alkyl chlorides, into condensed titanates which are insoluble in hydrocarbons and which are precipitated on the solid. The heat treatment is carried out until no further alkyl chlorides are split off. As a rule, a reaction time of 10 to 100 hours is required for this.

All the soluble reaction products are then removed by washing several times with a hydrocarbon, and a solid which is insoluble in the hydrocarbon and which contains magnesium and titanium, is obtained; this will be designated component A.

The polymerization catalyst to be used in accordance with the invention is prepared by bringing into contact with one another the component A and an organometallic compound of Groups I to III of the periodic system (component B).

It is preferable to use organoaluminum compounds as the component B. Suitable organoaluminum compounds are organoaluminum compounds containing chlorine, the dialkylaluminum monochlorides of the formula R_2^2AlCl or the alkylaluminum sesquichlorides of the formula $R_3^2Al_2Cl_3$ in which R^2 can be identical or different alkyl radicals having 1 to 16 carbon atoms. The following may be mentioned as examples: $(C_2H_5)_2AlCl$, $(iC_4H_9)_2AlCl$ and $(C_2H_5)_3Al_2Cl_3$.

It is particularly preferable to employ chlorine-free compounds as the organoaluminum compounds. Compounds suitable for this purpose are, firstly, the products from the reaction of aluminum trialkyls or aluminum dialkylhydrides with hydrocarbon radicals having 1 to 6 carbon atoms, preferably the reaction of $Al(iC_4H_9)_3$ or $Al(iC_4H_9)_2H$ with diolefins containing 4 to 20 carbon atoms, preferably isoprene. Aluminum isoprenyl may be mentioned as an example.

Secondly, chlorine-free organoaluminum compounds of this type are aluminum trialkyls AlR_3^3 or aluminum dialkylhydrides of the formula AlR_2^3H in which R^3 denotes identical or different alkyl radicals having 1 to 16 carbon atoms. Examples are $Al(C_2H_5)_3$, $Al(C_2H_5)_2H$, $Al(C_3H_7)_3$, $Al(C_3H_7)_2H$, $Al(iC_4H_9)_3$, $Al(iC_4H_9)_2H$, $Al(C_8H_{17})_3$, $Al(C_{12}H_{25})_3$, $Al(C_2H_5)(C_{12}H_{25})_2$ and $Al(iC_4H_9)(C_{12}H_{25})_2$.

It is also possible to employ mixtures of organometallic compounds of Groups I to III of the periodic system, particularly mixtures of different organoaluminum compounds. The following mixtures may be mentioned as examples: $Al(C_2H_5)_3$ and $Al(iC_4H_9)_3$, $Al(C_2H_5)_2Cl$ and

$Al(C_8H_{17})_3$, $Al(C_2H_5)_3$ and $Al(C_8H_{17})_3$, $Al(C_4H_9)_2H$ and $Al(C_8H_{17})_3$, $Al(iC_4H_9)_3$ and $Al(C_8H_{17})_3$, $Al(C_2H_5)_3$ and $Al(C_{12}H_{25})_3$, $Al(iC_4H_9)_3$ and $Al(C_{12}H_{25})_3$, $Al(C_2H_5)_3$ and $Al(C_{16}H_{33})_3$, $Al(C_3H_7)_3$ and $Al(C_{18}H_{37})_2(iC_4H_9)$ or $Al(C_2H_5)_3$ and aluminum isoprenyl (the reaction product of isoprene with $Al(iC_4H_9)_3$ or $Al(iC_4H_9)_2H$).

The component A and the component B can be mixed in a stirred kettle at a temperature of -30° C. to 150° C., preferably -10° to 120° C., before the polymerization. It is also possible to combine the two components directly in the polymerization kettle at a polymerization temperature of 20° to 200° C. The addition of the component B can, however, also be effected in two stages by pre-activating the component A with part of the component B at a temperature of -30° C. to 150° C. before the polymerization reaction, and adding the remainder of the component B in the polymerization reactor at a temperature of 20° to 200° C.

The polymerization catalyst to be used in accordance with the invention is employed for the polymerization of 1-olefins of the formula $R^4CH=CH_2$ in which R^4 denotes hydrogen or an alkyl radical having 1 to 10 carbon atoms, for example ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene or 1-octene. It is preferable to polymerize ethylene on its own or in the form of a mixture containing at least 70% by weight of ethylene and not more than 30% by weight of another 1-olefin of the above formula. In particular, ethylene is polymerized on its own, or a mixture containing at least 90% by weight of ethylene and not more than 10% by weight of another 1-olefin of the above formula is polymerized.

The polymerization is carried out in a known manner in solution, in suspension or in the gas phase, continuously or discontinuously, in a single stage or in several stages and at a temperature of 20° to 200° C., preferably 50° to 150° C. The pressure is 0.5 to 50 bar. Polymerization within the pressure range from 5 to 30 bar, which is of particular interest in industry, is preferred.

In this polymerization, the component A is used in a concentration, calculated as titanium, of 0.0001 to 1, preferably 0.001 to 0.5, mmole of Ti per liter of dispersion medium or per liter of reactor volume. The organometallic compound is used in a concentration of 0.1 to 5 mmoles, preferably 0.5 to 4 mmoles, per liter of dispersion medium or per liter of reactor volume. In principle, however, higher concentrations are also possible.

Suspension polymerization is carried out in an inert dispersion medium which is customary for the Ziegler low-pressure process, for example in an aliphatic or cycloaliphatic hydrocarbon; butane, pentane, hexane, heptane, isooctane, cyclohexane or methylcyclohexane may be mentioned as examples of such a hydrocarbon. It is also possible to use a gasoline or hydrogenated diesel oil fraction which has been carefully freed from oxygen, sulfur compounds and moisture. The molecular weight of the polymer is regulated in a known manner; it is preferable to use hydrogen for this purpose.

As a result of the high activity of the catalyst to be used, the process according to the invention produces polymers having a very low content of titanium and halogen and, therefore, extremely good values in the test for color stability and corrosion. It also makes it possible to prepare polymers having a very broad molecular weight distribution; the M_w/M_n values of the polymers are over 10.

A further decisive advantage of the process according to the invention can be seen in the fact that it makes it possible to prepare polymers having molecular weights which differ very greatly, merely by varying the concentration of hydrogen. For example, polymers having molecular weights above 2 million are formed in a polymerization in the absence of hydrogen, and polymers having molecular weights in the region of 30,000 are formed at hydrogen contents of 70% by volume in the gas space.

The polymers can be fabricated at high throughput rates by the extrusion and blow-extrusion process to give hollow articles, tubes, cables and films which have smooth surfaces.

By virtue of a special structural composition, the hollow articles and bottles produced from the polyolefins obtained in accordance with the invention are distinguished by a considerable lack of sensitivity to stress cracking.

Furthermore, the process according to the invention makes it possible to prepare, by suspension and gas phase polymerization, free-flowing polymer powders having high bulk densities, so that they can be processed further directly to give shaped articles without a granulation stage.

EXAMPLES

In the examples which follow, a hydrogenated diesel oil fraction having a boiling range of 130° to 170° C. is used for the preparation of the catalyst and for the polymerization.

The titanium content of the catalysts is determined colorimetrically (literature reference: G. O. Müller, *Praktikum der quantitativen chemischen Analyse* ["Practical manual of quantitative chemical analysis"], 4th edition (1957), page 243).

The melt index MFI is determined as specified in DIN No. 53,735 (E).

The Mw/Mn values are determined from the fractionation data of a gel permeation chromatograph at 130° C., using 1,2,4-trichlorobenzene as the solvent and extraction medium.

The intrinsic viscosity is determined as specified in DIN No. 53,728, sheet 4, using an Ubbelohde viscometer, with decahydronaphthalene as the solvent.

The density is determined as specified in DIN No. 53,479 and the bulk density as specified in DIN No. 53,468.

EXAMPLE 1

(a) Preparation of the component A

114.3 g of magnesium ethylate were dispersed, under a blanket of N₂, in 1.5 l of a diesel oil fraction in a 3 l four-necked flask equipped with a dropping funnel, a KPG stirrer, a reflux condenser and a thermometer. 332 g of titanium tetrachloride were added dropwise at 90° C. to this dispersion in the course of 2 hours. The mixture was then warmed to 130° C. and was stirred at this temperature for 60 hours. A gentle stream of N₂ was passed over the reaction mixture during the whole reaction time in order to expel gaseous reaction products, and this stream was then passed through a cold trap cooled with methanol/solid carbon dioxide. The evolution of gaseous reaction products was complete after 60 hours. 116 g of a water-white liquid of the following composition: Cl=55% by weight, C=37% by weight and H=8% by weight were collected in the cold trap. This was ethyl chloride. The reaction product was then

washed with the diesel oil fraction mentioned above, until the supernatant solution no longer contained any titanium.

After drying, the solid (component A) had the following analytical composition:

Ti 25.4% by weight

Mg 9.5% by weight

Cl 50.2% by weight

The Cl:Ti atomic ratio was 2.67.

(b) Pre-activation of the component A

19 g of the component A were made up to 190 ml with diesel oil, and 100 ml of an aluminum triisobutyl solution containing 1 mole of Al(iC₄H₉)₃ per l of solution were added at 20° C., while stirring. 45% by weight of the tetravalent titanium were reduced to titanium-(III) by this means.

(c) Polymerization of ethylene in suspension

100 l of diesel oil, 30 mmoles of aluminum triisobutyl and 8.7 ml of the dispersion described under (b) were charged to a 150 l kettle. 5 kg per hour of ethylene and sufficient H₂ to give an H₂ content of 55% by volume in the gas space were then passed in, at a polymerization temperature of 85° C. After 6 hours the polymerization was terminated at a pressure of 25.3 bar, by releasing the pressure. The suspension was filtered and the polyethylene powder was dried by passing hot nitrogen over it.

28.7 kg of polyethylene were obtained. This corresponds to a catalyst activity of 50.4 kg of polyethylene/g of catalyst solid (component A) or 9.5 kg of polyethylene/mole of Ti. The polyethylene powder had an MFI 190/5 of 0.54 g/10 minutes. The breadth of molecular weight distribution Mw/Mn was 22 and the MFI 190/15/MFI 190/5 was 11.5. The density of the powder was 0.955 g/cm³ and its bulk density was 0.49 g/cm³.

EXAMPLE 2

Polymerization of ethylene in suspension

100 mmoles of aluminum triisobutyl and 2.2 ml of the dispersion described in Example 1(b) were charged to the kettle under the same conditions as those described in Example 1(c). 5 kg per hour of ethylene were then passed in at a polymerization temperature of 75° C. After 6 hours the polymerization was terminated at a pressure of 24.8 bar, by releasing the pressure. The suspension was filtered and the polyethylene powder was dried by passing hot nitrogen over it. 27.9 kg of polyethylene were obtained. This corresponds to a catalyst activity of 194 kg of polyethylene/g of catalyst solid or 36.5 kg of polyethylene/mole of Ti. The polyethylene powder had an intrinsic viscosity of 2,400 ml/g; this corresponds to a molecular weight of 2 million. Its bulk density was 0.45 g/cm³.

EXAMPLE 3

Polymerization of ethylene in suspension

100 mmoles of aluminum triisobutyl and 29 ml of the dispersion described in Example 1(b) were charged to the kettle under the same conditions as those described in Example 1(c). 4 kg per hour of ethylene and sufficient H₂ to give an H₂ content of 75% by volume in the gas space were then passed in at a polymerization temperature of 85° C. After 6 hours the polymerization was terminated at a pressure of 25.6 bar, by releasing the

pressure. The suspension was filtered and the polyethylene powder was dried by passing hot nitrogen over it. 23.6 kg of polyethylene were isolated. This corresponds to a catalyst yield of 12.4 kg of polyethylene/g of catalyst solid or 2.3 kg of polyethylene/mole of Ti. The polyethylene had an MFI 190/5 of 105 g/10 minutes, an intrinsic viscosity of 110 ml/g, a density of 0.965 g/cm³ and a bulk density of 0.50 g/cm³. The breadth of molecular weight distribution Mw/Mn was 25.

EXAMPLE 4

Copolymerization of ethylene and 1-decene in suspension

750 ml of hexane, 5 mmoles of aluminum isoprenyl and 2.9 mg of the component A obtained in accordance with Example 1(b) were charged to a 1.5 l steel autoclave. H₂ was then injected at 8 bar, and ethylene at 14 bar, at a polymerization temperature of 85° C. The ethylene was subsequently metered in at such a rate that a total pressure of 22 bar was maintained. 20 ml per hour of 1-decene were metered in at the same time. The experiment was discontinued after 6 hours. The copolymer was isolated by filtration and dried in a vacuum drying cabinet. 156 g of copolymer were obtained. This corresponds to a catalyst yield of 53.8 kg of polymer/g of catalyst solid or 10.1 kg of polymer/mole of Ti. The ethylene/1-decene copolymer had a melt index MFI 190/5 of 0.68 g/10 minutes and a density of 0.950 g/cm³.

EXAMPLE 5

Copolymerization of ethylene and 1-hexene in suspension

360 l of hexane, 360 mmoles of aluminum isoprenyl and 58 ml of the dispersion described in Example 1(b) were initially taken in a 500 l kettle. 17 kg/hour of ethylene, 2 l/hour of 1-hexene and sufficient H₂ to set up an H₂ content of 45% by volume in the gas space were then passed in at a polymerization temperature of 85° C.

After 6 hours the polymerization pressure had risen to 8.2 bar, and the polymerization was discontinued by releasing the pressure. The polymer powder was isolated by filtration and was dried with hot nitrogen. 100.4 kg of polymer were obtained. This corresponds to a catalyst yield of 26.4 kg of polymer/g of catalyst solid or 5.0 kg of polymer/mole of Ti.

The ethylene/1-hexene copolymer had a melt index MFI 190/5 of 0.9 g/10 minutes, an MFI 190/15/MFI 190/5 ratio of 9.8, a density of 0.942 g/cm³ and a bulk density of 0.42 g/cm³.

Bottles were produced from the powder on a blow-molding apparatus for bottles (extruder screw: D=60 mm). A very high output, 62 kg/hour, was obtained at a screw speed of 40 r.p.m. The bottles had a very smooth surface and had a very high resistance to stress cracking, over 1,000 hours, in the Bell stress cracking test.

EXAMPLE 6

Copolymerization of ethylene and 1-butene in suspension

720 mmoles of aluminum triisobutyl and 58 ml of the dispersion described in Example 1(b) were charged under the same conditions as those described in Example 5. 17 kg per hour of ethylene and 4 l per hour of 1-butene were added at 65° C. Sufficient H₂ was passed

in to give a concentration of 40% by volume of the latter in the gas space. After 6 hours the polymerization was discontinued at a final pressure of 6.7 bar, by releasing the pressure.

The suspension was cooled to room temperature and the solid was isolated by filtration and dried with hot N₂.

108.4 kg of product having an MFI 190/5 of 1.8 g/10 minutes, an MFI 190/15/MFI 190/5 of 10.4, a density of 0.920 g/cm³ and a bulk density of 0.30 g/cm³ were obtained. This corresponds to a catalyst yield of 28.5 kg of copolymer/g of catalyst solid or 5.4 kg of copolymer/mole of Ti.

EXAMPLE 7

Polymerization of ethylene in the gas phase

500 g of polyethylene powder (MFI 190/5=1.5 g/10 minutes; bulk density=0.45 g/cm³) were initially taken in a 20 l horizontal reactor equipped with a stirrer operating close to the wall. The reactor was freed from air by being evacuated several times and flushed for several hours with ethylene and was then warmed to 80° C. 50 mmoles of aluminum triisobutyl and 94.3 mg of the catalyst component A prepared in accordance with Example 1(a) were added to the reactor.

400 g/hour of ethylene and sufficient hydrogen to keep the proportion of hydrogen in the gas space at 30% by volume during the polymerization were passed in. The pressure rose to 15 bar during the reaction time. After 12.5 hours the polymerization was discontinued. 5.4 kg of polyethylene having an MFI 190/5 value of 0.6 g/10 minutes were obtained. This corresponds to a catalyst yield of 52 kg of polyethylene/g of catalyst solid or 9.8 kg of polyethylene/mole of Ti.

COMPARISON EXAMPLE A

(a) Preparation of the component A

114.3 g of magnesium ethylate were dispersed, under a blanket of N₂, in 1.5 l of a diesel oil fraction in a 3 l four-necked flask equipped with a dropping funnel, a KPG stirrer, a reflux condenser and a thermometer. 332 g of titanium tetrachloride were added dropwise at 90° C. to this dispersion in the course of 2 hours. The reaction product was then washed with the diesel oil fraction until the supernatant solution no longer contained any titanium. After drying, the solid (component A) had the following analytical composition:

Ti 4.9% by weight
Mg 19.8% by weight
Cl 61.3% by weight.

(b) Pre-activation of the component A

98 g of the component A were suspended in sufficient diesel oil to give a volume of suspension of 190 ml, and 100 ml of an aluminum triisobutyl solution containing 1 mole of Al(iC₄H₉)₃ per 1 l were added at 20° C., while stirring. 52% by weight of the tetravalent titanium were reduced to titanium-(III) by this means.

(c) Polymerization of ethylene in suspension

100 l of hexane, 30 mmoles of aluminum triisobutyl and 14.5 ml of the suspension described under (b) were charged to a 150 l kettle. 5 kg/hour of ethylene and sufficient H₂ to set up a hydrogen content of 30% by volume in the gas space were then passed in at 85° C. After 6 hours the polymerization was discontinued at a pressure of 4.6 bar, by releasing the pressure. 29.6 kg of

polyethylene were obtained. This corresponds to a catalyst yield of 6.1 kg/g of catalyst solid or 5.9 kg of polyethylene/mmole of Ti.

The product had an MFI 190/5 value of 1.6 g/10 minutes, an MFI 190/15/MFI 190/5 value of 5.2, a density of 0.956 g/cm³ and a bulk density of 0.42 g/cm³. The product had a narrow molecular weight distribution: Mw/Mn=4.7.

An output of 43 kg/hour was obtained at a screw speed of 40 r.p.m. when processing the powder on the blow-molding apparatus for hollow articles also used in Example 5. The bottles had a rough surface, since melt fracture occurred when they were processed. The resistance to stress cracking of the bottles in the Bell test was 68 hours.

(d) Polymerization of ethylene in suspension

100 l of diesel oil, 30 mmoles of aluminum triisobutyl and 8.7 ml of the dispersion described under (b) were charged to a 150 l kettle. 5 kg per hour of ethylene and sufficient H₂ to give an H₂ content of 55% by volume in the gas space were then passed in at a polymerization temperature of 85° C. After 6 hours the polymerization was terminated at a pressure of 20.4 bar, by releasing the pressure. The suspension was filtered and the polyethylene powder was dried by passing hot nitrogen over it.

28.2 kg of polyethylene were obtained. This corresponds to a catalyst activity of 9.6 kg of polyethylene/g of catalyst solid or 9.4 kg of polyethylene/mmole of Ti. The polymer powder had an MFI 190/5 of 28 g/10 minutes. The breadth of molecular weight distribution Mw/Mn was 4.6 and the MFI 190/15/MFI 190/5 was 5.4. The density of the powder was 0.960 g/cm³ and its bulk density was 0.41 g/cm³.

EXAMPLE 8

(a) Preparation of the component A

114.3 g of magnesium ethylate were dispersed, under a blanket of N₂, in 1.5 l of a diesel oil fraction in a 3 l four-necked flask equipped with a dropping funnel, a KPG stirrer, a reflux condenser and a thermometer. 569 g of titanium tetrachloride were added dropwise at 90° C. to this dispersion in the course of 2 hours. The mixture was then warmed to 130° C. and stirred at this temperature for 60 hours. A gentle stream of N₂ was passed over the reaction mixture during the whole reaction time in order to expel gaseous reaction products, and this stream was then passed through a cold trap cooled with methanol/solid carbon dioxide. The evolution of gaseous reaction products was complete after 60 hours. 107 g of a water-white liquid of the following composition: Cl=55% by weight, C=37% by weight and H=8% by weight were collected in the cold trap. This was ethyl chloride. The reaction product was then washed with the diesel oil fraction until the supernatant solution no longer contained any titanium.

After drying, the solid (component A) had the following analytical composition:

Ti 24.7% by weight

Mg 9.7% by weight

Cl 51.2% by weight.

The Cl:Ti atomic ratio was 2.80.

(b) Pre-activation of the component A

19.4 g of component A were made up to 190 ml with diesel oil, and 100 ml of an aluminum triisobutyl solution containing 1 mole of Al(iC₄H₉)₃ per 1 l were added at 20° C., while stirring. 47% by weight of the tetra-

lent titanium were reduced to titanium-(III) by this means.

(c) Polymerization of ethylene in suspension

100 l of diesel oil, 25 mmoles of aluminum triisobutyl and 8.0 ml of the dispersion described under (b) were charged to a 150 l kettle. 5 kg per hour of ethylene and sufficient H₂ to give an H₂ content of 55% by volume in the gas space were then passed in at a polymerization temperature of 85° C. After 6 hours the polymerization was terminated at a pressure of 22.4 bar, by releasing the pressure. The suspension was filtered and the polyethylene powder was dried by passing hot nitrogen over it.

27.5 kg of polyethylene were obtained. This corresponds to a catalyst activity of 51.4 kg of polyethylene/g of catalyst solid or 10 kg of polyethylene/mmole of Ti. The polyethylene powder had an MFI 190/5 of 0.94 g/10 minutes. The breadth of molecular weight distribution Mw/Mn was 26 and the MFI 190/15/MFI 190/5 was 11.9. The density of the powder was 0.956 g/cm³ and its bulk density was 0.47 g/cm³.

EXAMPLE 9

(a) Preparation of the component A

142.3 g of magnesium isopropylate were dispersed, under a blanket of N₂, in 1.0 l of a diesel oil fraction in a 3 l four-necked flask equipped with a dropping funnel, a KPG stirrer, a reflux condenser and a thermometer. 285 g of titanium tetrachloride were added dropwise at 75° C. to this dispersion in the course of 4 hours. The mixture was then warmed to 110° C. and was stirred at this temperature for 45 hours. A gentle stream of N₂ was passed over the reaction mixture during the whole reaction time in order to expel gaseous reaction products, and this stream was then passed through a cold trap cooled with methanol/solid carbon dioxide. The evolution of gaseous reaction products was complete after 60 hours. 156 g of water-white liquid of the following composition: Cl=45% by weight, C=46% by weight and H=8.9% by weight were collected in the cold trap. This was isopropyl chloride. The reaction product was then washed with the diesel oil fraction mentioned above, until the supernatant solution no longer contained any titanium.

After drying, the solid (component A) contained the following:

Ti 26.6% by weight

Mg 9.0% by weight

Cl 52.5% by weight.

The Cl:Ti atomic ratio was 2.67.

(b) Polymerization of ethylene in suspension

100 l of diesel oil, 100 mmoles of aluminum isoprenyl and 900 mg of the catalyst solid described under (a) were charged to a 150 l kettle. 5 kg per hour of ethylene and sufficient H₂ to give an H₂ content of 55% by volume in the gas space were then passed in at a polymerization temperature of 85° C. After 6 hours the polymerization was terminated at a pressure of 23.8 bar, by releasing the pressure. The suspension was filtered and the polyethylene powder was dried by passing hot nitrogen over it.

29.1 kg of polyethylene were obtained. This corresponds to a catalyst activity of 32.3 kg of polyethylene/g of catalyst solid or 5.8 kg of polyethylene/mmole of Ti. The polyethylene powder had an MFI 190/5 of 0.36 g/10 minutes. The breadth of molecular

weight distribution Mw/Mn was 28 and the MFI 190/15/MFI 190/5 was 12.7. The density of the powder was 0.954 g/cm³ and its bulk density was 0.39 g/cm³.

EXAMPLE 10

(a) Preparation of the component A

250.3 g of Na₂[Mg(OC₂H₅)₄](H. Meerwein and T. Bersin, Liebigs Annalen der Chemie 476, 113 [1929]) were dispersed, under a blanket of N₂, in 2.0 l of a diesel oil fraction in a 3 l four-necked flask equipped with a dropping funnel, a KPG stirrer, a reflux condenser and a thermometer. 759 g of titanium tetrachloride were added dropwise at 80° C. to this dispersion in the course of 4 hours. The mixture was then warmed to 145° C. and stirred at this temperature for 45 hours. A gentle stream of N₂ was passed over the reaction mixture during the whole reaction time in order to expel gaseous reaction products, and this stream was then passed through a cold trap cooled with methanol/solid carbon dioxide. The evolution of gaseous reaction products was complete after 60 hours. 118 g of a water-white liquid of the following composition: Cl=55% by weight, C=37% by weight and H=8% by weight were collected in the cold trap. This was ethyl chloride. The reaction product was then washed with the diesel oil fraction mentioned above until the supernatant solution no longer contained any titanium.

After drying, the solid (component A) had the following analytical composition:

Ti 16.9% by weight
Mg 6.6% by weight
Cl 52.9% by weight

(b) Polymerization of ethylene in suspension

100 l of diesel oil, 30 mmoles of aluminum triisobutyl and 1,417 mg of the catalyst solid described under (a) were charged to a 150 l kettle. 5 kg per hour of ethylene and sufficient H₂ to give an H₂ content of 65% by volume in the gas space were then passed in at a polymerization temperature of 85° C. After 6 hours the polymerization was terminated at a pressure of 21.7 bar, by releasing the pressure. The suspension was filtered and the polyethylene powder was dried by passing hot nitrogen over it. corresponds to a catalyst activity of 19.9 kg of polyethylene/g of catalyst solid or 7.1 kg of polyethylene/mmmole of Ti. The polyethylene powder had an

MFI 190/5 of 3.2 g/10 minutes. The breadth of molecular weight distribution Mw/Mn was 21 and the MFI 190/15/MFI 190/5 was 10.5. The density of the powder was 0.955 g/cm³ and its bulk density was 0.49 g/cm³.

5 We claim:

1. A process for the polymerization of ethylene or an olefin mixture comprising at least 70% by weight of ethylene and not more than 30% by weight of a 1-olefin of the formula R⁴CH=CH₂ in which R⁴ denotes an alkyl radical having 1 to 10 carbon atoms, in the presence of a catalyst comprised of the product from the reaction of a magnesium alcoholate of the formula Mg(OR)₂, in which R denotes identical or different alkyl radicals having 1 to 6 carbon atoms, with 1 to 5 moles titanium tetrachloride for each mole of magnesium alcoholate (component A) and an organometallic compound of Groups I to III of the periodic system (component B), which comprises carrying out the polymerization in the presence of a catalyst in which the component A has been prepared by a procedure in which, in a first reaction stage, a magnesium alcoholate has been reacted with titanium tetrachloride in a hydrocarbon at a temperature of 50° to 100° C., the reaction mixture formed is subjected, in a second reaction stage, to a heat treatment for a period of about 10 to 100 hours at a temperature of 110° to 200° C., with evolution of alkyl chloride until no further alkyl chloride is split off, and the solid is then freed from soluble reaction products by washing several times with a hydrocarbon.

2. The process as claimed in claim 1, wherein the component A is prepared by reacting, in the first reaction stage, a complex magnesium alcoholate which, as well as magnesium, contains at least one metal of the 1st to 4th main group of the periodic system, with titanium tetrachloride in a hydrocarbon at a temperature of 50° to 100° C., subjecting, in a second reaction stage, the reaction mixture which has been formed to a heat treatment at a temperature of 110° to 200° C. until no further alkyl chloride is split off, and then freeing the solid from soluble reaction products by washing it several times with a hydrocarbon.

3. A process according to claim 1, wherein the resulting polyethylene or ethylene/1-olefin copolymer has an Mw/Mn value greater than 10.

* * * * *

50

55

60

65